Relative usefulness of the Bayer ratio as an indicator of the hardness of different coatings

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ABSTRACT

Purpose: To show that with better performance of scratch-resistant coatings on plastic lenses, the use of the Bayer ratio does not appropriately discriminate between recently introduced products.

Methods: Nine groups of 5 to 10 CR-39 lenses were ordered with various scratch-resistant treatments. All the lenses underwent the Bayer test on the same apparatus. Haze was measured using a Cary5000 spectrophotometer equipped with an integrating sphere.

Results: The lens groups with the latest generation of anti-scratch treatments show a significant decrease in diffusion. The variability of the Bayer ratio increases depending on whether the quotient is obtained by calculating the ratio using the minimal haze values or the maximum haze values. When the Bayer ratio is greater than 10, it no longer discriminates between the products satisfactorily.

Conclusions: This test, or others, will inevitably have to be refined to increase precision and give a better perspective of the quality of the next generation of scratch-resistant coatings.

Keywords: Bayer ratio; coatings; anti-scratch; antireflective; ophthalmic lenses

Introduction

In the early 70's, it was fairly common to think that the effectiveness of scratch-resistant treatments was a function of the material's hardness, defined by the resistance to local penetration of the material. When CR-39 entered the ophthalmic lens market, it suffered from comparison with highly scratch-resistant ophthalmic crown glass. A test developed by Essilor's international research laboratory evaluated scratch resistance by using a diamond tipped stylus which scratched the lens.[1,2] The modified lead pencil test, which consists of pushing pencils of different hardness into the sample and then identifying the trace generated, was also used by Essilor. These two tests ensured a reproducibility which could take into account various materials and different variables such as the geometry of the lens, and the pressure exerted on the material by the diamond tip of the stylus.

Other procedures were developed to compare and quantify scratch resistance. The Tumble Abrasion Test (TAT), introduced in 1974, placed the lens being tested in a barrel-shaped container to which an abrasive powder was added.[3] During rotation of the container, abrasions were produced on the surface of the lens. The steel wool test was frequently used to show customers the effectiveness of scratch-resistant treatments.[3] This test was unreliable, subjective and difficult to control. Wilkinson (1984) reported the use of an instrument by a group of scientists at Sheffield City Polytechnic, to test various surface coatings on CR-39 lenses.[4] At the same time, Honson et al. (1986) developed an apparatus based on the friction method.[5] Later, Obstfeld et al. (1991) revised the principle of Honson by using a modified record player.[6] Currently, a standard test used to measure the effectiveness of scratch-resistant treatments is the Bayer ratio.[7] The apparatus is designed so that a standard lens, not having any surface treatment and made of CR-39, undergoes the test at the same time as the lens being tested. Set side-by-side, the lenses with the same base curve are mounted in a pan with their convex surface in contact with an abrasive material. Abrasions are caused by the oscillation of the abrasive media. The quantification of the abrasion resistance is based on the measurement of the loss of transparency of the lenses, i.e. haze, using a spectrophotometer.

The Bayer ratio is the quotient of the gain in measured haze of the uncoated hard resin control lens to the gain in haze of the test lens after a number of cycles in an oscillating pan covered in abrasive material. The higher the Bayer ratio, the better is the abrasion resistance of the lens being tested.

Over the last several decades, advances in chemistry have allowed the use of hardening coatings, polysiloxanes or acrylic resins on organic lenses, all still widely used today. The combination of quartz and polymers in early scratch-resistant lenses generated cracks and was quickly replaced. The application of hard coatings is now done primarily by dip or spin processes.[8] The basic treatments, simpler and quicker, are done by spin; the higher performance treatments are done by dipping. This last technique takes longer and requires control of many environmental variables in order to obtain maximum durability.

The advent of anti-reflection treatments gives rise to new challenges in scratch resistance. In the late 1980's, hard coatings and nanocomposite coatings made possible the mechanical transition between the anti-reflection coat (hard and brittle) and the polymer (flexible and deformable). The silica nanoparticules are put in suspension in a liquid of structure similar to polysiloxane, which has the properties of a hard coating and is deposited on the lenses by either dip or spin. This remarkable coating has, on the one hand, a great resistance to depression, which will prevent the anti-reflection coat deposited on top to become deformed beyond the rupture limit, and on the other hand, a flexibility high enough to follow the polymer in its deformation without rupture. Also, having an extremely low coefficient of friction provides an increase in the abrasion resistance.[8] Today, antireflective (AR) treatment by vacuum deposit, is recognized as being the most reproducible technique to ensure high quality performance coatings.

The purpose of this study was to show the limits of the Bayer ratio method to evaluate lenses with the latest generation of highly effective scratch-resistant treatments using spectrophotometry equipment.

Methods

Lenses

Nine groups of five CR-39 lenses, apart from one group containing only three lenses, were ordered with various scratch-resistant treatments. Three groups (Hoya HV, Zeiss C, Essilor CF) represent top-of-the-range products from different suppliers, and the four other groups are products that have been on the market for several years, two of which do not have anti-reflection treatment.
Two other groups, composed of untreated CR-39 and untreated crown glass were also ordered (Table 1).

TABLE 1

Details of lenses used for comparison of Bayer Test

Groups	Manufacturers	Materials	Coatings	Antireflective
Ess CR39	Essilor	CR-39	none	none
EssTT	Essilor	CR-39	truetint	none
Ess TD2	Essilor	CR-39	TD2	none
Sola Tef	Sola	CR-39	yes	Teflon
Ess CA	Essilor	CR-39	yes	Crizal Alize
Hoya HV	Hoya	CR-39	yes	HiVision
Zeiss C	Zeiss	CR-39	yes	Carat
Ess CF	Essilor	CR-39	yes	Crizal Forte
Ess Glass	Essilor	Glass	none	none

Measurements

All the lenses underwent the Bayer test on the same apparatus, with a protocol derived from the document Bayer (AR Council; Method for the Modified Bayer Test, July 1999). Basically, the test lenses and the reference lens are placed in a Bayer pan matching the configuration of the protocol of the AR Council. The lenses perform 600 cycles of abrasion in presence of 500g of alumdum abrasive media.

The measurement of haze was done using the Cary5000 spectrophotometer (Varian, Mulgrove, Australia) equipped with an integrating sphere (internal diffuse reflectance accessory). Calculation is integrated into the Varian software designed for the apparatus. All measurements were done under the same conditions, by the same technician. More specifically, haze is the percentage of transmitted light passing through a sample that deviates from the incident beam by forward scattering. According to ASTM Method D1003, haze is calculated as follows:

Haze, % = $T_d/T_t * 100$

where:

T_d = diffuse luminous transmittance = $[T_4 - T_3 (T_2/T_1)] / T_1$

T_t = total transmittance = T_2/T_1

The ASTM standard test method for measuring the haze and luminous transmittance of transparent plastics (D1003-61) requires 4 scans to be collected with varying configurations of the sample, light trap and the white reference plate. All scans are performed using an integrating sphere (Diffuse Reflectance Accessory).

T_1 = incident light: Scan with the white reference plate in position (equivalent to a baseline)

T_2 = total light transmitted by sample: Scan with the sample and the white reference plate in position.

T_3 = light scattered by the integrating sphere: Scan with the sample and the white reference plate removed. The light should pass straight through the sphere.

T_4 = light scattered by the integrating sphere and sample: Scan with the sample in position and the white reference plate removed. The light will pass through the sample and out of the sphere into the sample compartment.

Statistical Analysis

We used univariate ANOVA combined with the Tukey-Kramer test of comparison to determine which average haze values were significally different from the others. Then, we calculated the Bayer ratio taking into account the mean results of each group.

TABLE 2

Haze (in percentage) and Bayer ratio by lens group

		Haze (percentge)				Bayer ratio			
group	n	mean	std dev	min	max	mean	std dev	min	max
Ess CR39	5	15.96	0.58	15.44	16.87	1.01	0.05	0.92	1.09
Ess TT	5	6.27	0.23	6.08	6.79	2.55	0.16	2.28	2.78
Ess TD2	5	3.76	0.27	3.45	4.17	4.24	0.35	3.70	4.89
Sola Tef	5	4.70	0.45	3.91	4.99	3.40	0.39	3.09	4.31
Ess Ca	5	1.65	0.22	1.40	1.93	9.66	1.19	7.99	12.03
Hoya HV	3	2.46	0.66	1.70	2.92	6.50	2.56	5.30	9.95
Zeiss C	5	3.14	0.35	2.68	3.47	5.08	0.58	4.45	6.29
Ess CF	5	1.69	0.44	1.04	2.65	10.33	4.14	5.82	17.18
Ess Glass	5	1.75	0.81	0.93	3.57	13.84	3.90	4.32	18.24

Results

Table 2 shows the haze for each group of lenses. The mean and standard deviation is calculated for each group of five lenses. The minimal and maximal values in each group are also showed. We found that the quantity of haze for the untreated CR-39 is higher than that observed for treated lenses.

The analysis of variance showed a significant difference in the average haze between groups (ANOVA F=355,7; df=8; p<0,001). Moreover, the statistical comparison of the averages according to Tukey-Kramer, makes it possible to distinguish five levels of difference (Table 3). Obviously, the untreated CR-39 stands out, followed by the treatment by spin (Essilor true tint). The results of groups Ess TD2 and Sola Teflon reflect older treatments, whereas the last two levels show groups representing the latest generation of treated lenses. There is overlapping of levels for groups Essilor TD2 and Hoya HiVision.

By calculating the quotient of the average haze from Table 2, we obtain the results illustrated in Figure 1, which are in fact the Bayer ratio calculated from minimum and maximum measurements for each group.

Discussion

This study shows that all treatments produce an increase in scratch resistance, however light diffusion, as expressed by the percentage haze, shows much variation. In the most extreme cases, the absence of treatment on CR-39 lenses (untreated) leads to a high level of light diffusion, which interferes with the transparency, whereas crown glass (Ess glass) exhibits very low diffusion, which reflects its exceptional hardness.

The groups with the latest generation anti-scratch treatments show a significant decrease in haze; within this level of contemporary lenses (Hoya HV, Essilor Crizal Forte and Crizal Alizé), the statistical differences between the thresholds in haze are not significant. This is explained partly by very low haze measurements associated with respectively notable intra group variations. Moreover, from these results, the calculation of the Bayer ratio between the group of untreated CR-39 lenses and the same groups of treated lenses show that the variability of this ratio increases quite a bit, depending on whether the quotient is obtained by calculating the ratio using the minimal or the maximal haze values, as shown in Table 2. Figure 1 illustrates quite well that for a Bayer ratio of 10 and higher, the confidence intervals for the values of each group intersect so much that the results no longer allow one to satisfactorily discriminate the products.

TABLE 3

Comparisons of average haze with the Tukey-Kramer method

Groups	Levels					Average	
Ess CR39	A					15.96	
EssTT		B				6.27	
Sola Tef			C			4.70	
Ess TD2			C	D		3.76	
Zeiss C				D		3.14	
Hoya HV				D	E	2.46	
Ess Glass					E	1.77	
Ess CF					E	1.71	
Ess CA					E	1.65	

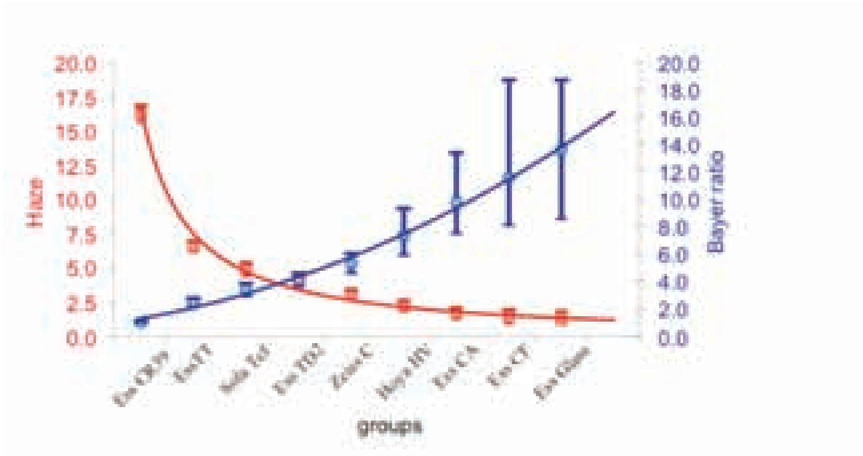

Figure 1: *Blue: means and standard deviation of the Bayer ratio for each group of lenses. Red: percent haze.*

Since the haze in the products that have been scratched following the Bayer test protocol is decreasing, as the lens manufacturers develop new treatment technologies, the comparison with an untreated lens subjected to the same procedure becomes obsolete. The quotient of the haze values obtained is projected to very high values, but so is the variation. Consequently, the uncertainty zone increases and there is an overlaping of the Bayer ratio of the groups under comparison.

The companies that manufacture the latest generation of multi-layer treatments push the limits of the controls of treatment performance. This is good news because several studies have already shown the positive impact of unscratched lenses on visual performance. [9, 10] However, in terms of quantification of the scratches, the current tests (the Bayer, steel wool and Taber tests, to name a few) will inevitably have to be refined to increase their precision. This will allow a better resolution of the results and will guide eye care providers in choosing a quality treatment for the visual performance and comfort of the wearer. For example, it would be interesting to use a glass lens instead of a CR-39 untreated lens as the reference lens. Haze on glass would be closer to the haze on a latest generation multi-layer coated lens. Another modification of the test would be to increase the abrasion time, since new coatings are more resistant.

But finally, in parallel with new tests and procedures to adequately discriminate the latest generation treatments, we should pay special attention to the sources of errors resulting from the handling of the lens in scratch-resistant treatments and measurement techniques. These two crucial steps in the protocol can involve uncertainties, therefore there is a need to work out solid statistical protocols.

Notes

All lenses were provided by Essilor USA, subsidiary of Essilor International. We would like to thank Dr. Gabriel Keita, from Essilor, for his help with this work.

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